Oxidation Number +1

Chloride

Hypochlorite

Oxidation Number +3

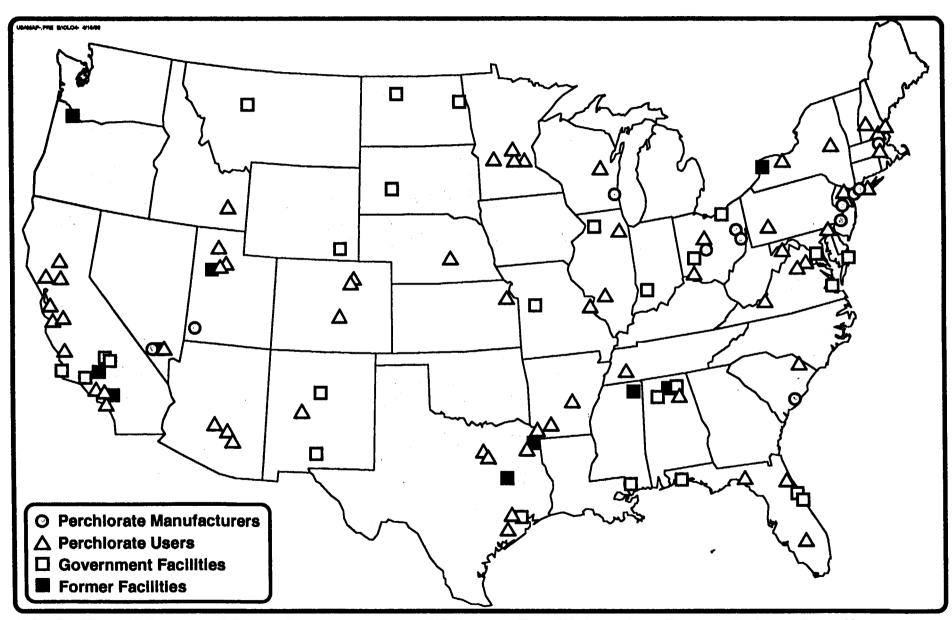
Chlorite

Oxidation Number +5

Chlorate

Oxidation Number +7

Perchlorate



U. S. Perchlorate Manufacturers and Users Facilities for Propulsion Applications

# **Perchlorate History**

- **Uses** Solid Rocket Fuel Component
  - Up to 90% of Rocket Fuel Mass
  - Pyrotechnics, Cattle Feed?
  - Medicine for Hyperthyroidism (Graves Disease) in 1950's

#### Chemistry

- Highly Oxidized Chlorine
- Dissociated Salt, Anion
- Highly Soluble, Mobile, Stable
- Ammonium, Potassium, Sodium salts

#### **EPA Region 9**

- Possible Probl m at Superfund Site
   In 1985, But Analytical Failure
  - High Levels in Sacramento SF Site
  - 1992 Provisional Reference Dose
  - 1995 Revision

# Perchlorate History

#### 1997 Analytical Method Development

#### **Testing for Perchlorate**

- Standard Method (IC) for >400ppb
- CA method to 4 ppb in February 1997
- Based on EPA Reference Dose

Discovery in Water Supply Wells in Rancho Codova

**Testing Throughout California** 

# PERCHLORATE (CIO<sub>4</sub>-)

Uses - Solid Rocket Fuel Component

- **Chemistry** Highly Oxidized Chlorine
  - Dissociated Salt, Anion
  - Highly Soluble, Mobile, Stable
- **Toxicology** Thyroid Disruption (Children!)
  - Poorly Studied, Used as Drug
  - Provisional Reference Dose (Range 4 to 18 ppb, KClO₄)
- Regulation Not Regulated (SDWA, RCRA,CERCLA)
  - California Interim Action Level (18 ppb)

### **Testing for Perchlorate**

- Standard Method for >400ppb
- CA method to 4 ppb in 1997

## **PERCHLORATE**

### **Discovery in Water Supply Wells**

- CA DHS Initiative
- February Discovery in Sacramento (Aerojet)
- March-June Survey in California
- Results Show Ten Separate CA Sources

### Discovery in Colorado River (5-9 ppb)

- Metropolitan Water District of So. California
- Traced to Lake Mead, 150 miles Upriver
- Water Supply for NV, AZ, CA, tribes

#### Major Sources in Nevada

- Kerr-McGee (BMI Complex)
- PEPCON Site (Destroyed 1988)
- Groundwater levels > 1,000 mg/L

### Source(s) in Utah - Alliant (Hercules)

#### **Sources Nationwide**

#### CULTELL MULIVILIES

#### Site Remediation

- Superfund Sites
- RCRA Sites
- State Sites (Nevada)

# Communication with States, EPA (letters) Occurrence

#### **Toxicology Research**

- Air Force and Private Funding (\$1.4 M)
- EPA Review by Sept 1998
- External Peer Review by Oct 1998

#### **Treatment Technologies**

- East Valley Water District...AWWARF
   (\$2 Million from EPA's OST Budget)
- Tech Support, Reviewing \$F Reports
- Other Efforts -San Gabriel, USAF, MWD

#### **Analytical Methods**

- Tech Support, EPA NERL Lab

# **Community Concerns**

#### Congress

- House and Senate
- No one in favor of rocket fuel in DW

#### **States and Tribes**

- California High interest, Regulations
- Nevada More general support

### **Local Water Suppliers**

- Desperate for Information
- Active lobbying of Congress, states
- Want to say, "Water is safe!"

#### Media

- Local news, Trade publications, Political
- Las Vegas stories, Press conferences
- Pressure from local officials ??

#### **Citizens Groups**

- Dispute that 18 ppb is "safe"
- Distrust "PRPs" to do toxicology
- Children, Elderly, EJ (Cost of treatment)

#### Individuals

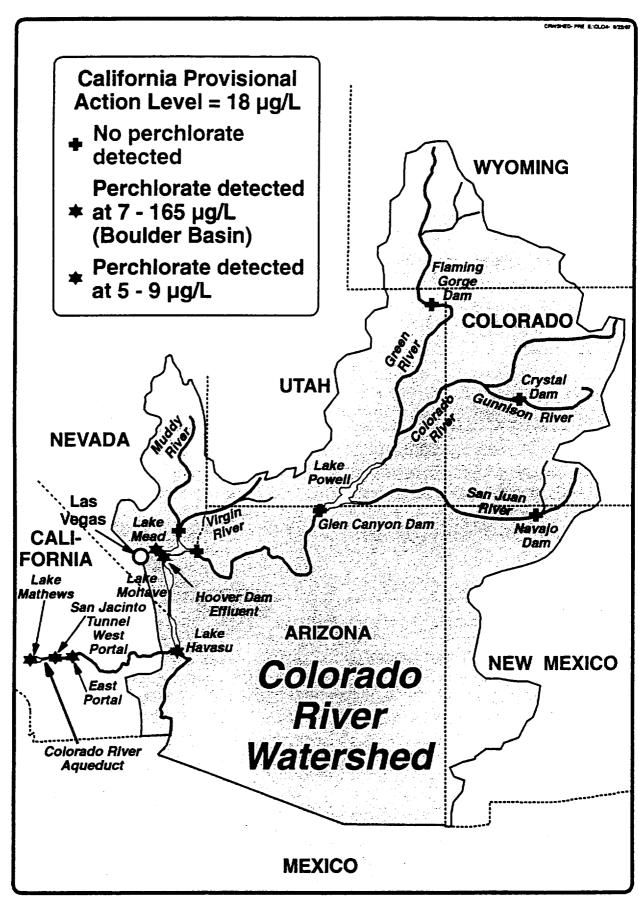
- Need information, explanations
- Lake Havasu, Redlands, Sacto Fireman

# COLORADO RIVER and LAKE MEAD

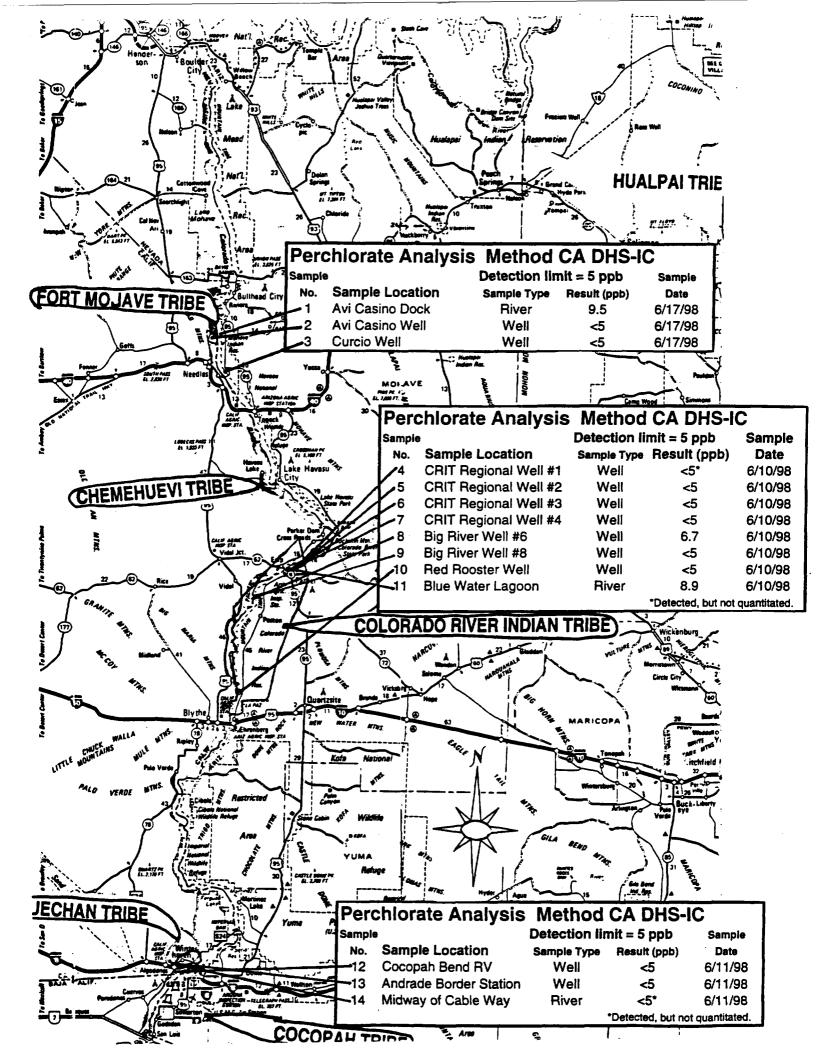


- Southern California Aqueduct
- Lake Havasu (Colorado River)
- Lake Mead
- Non-Detect Upstream





Perchlorate Detection in the Colorado River Watershed





#### UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION IX 75 Hawthorne Street

San Francisco, CA 94105

In Reply Use Mail Code WTR-6 July 2, 1998

Dear Tribal Leader.

Enclosed is a copy of testing results from June 1998 sampling for perchlorate in the Colorado River and from public water supply wells located adjacent to the river, which EPA considered vulnerable to perchlorate contamination. EPA arranged for the sampling and testing with the assistance of the Indian Health Service (IHS) and the California Department of Health Services (DHS).

This testing was completed to provide Tribal populations, the IHS, EPA and other stakeholders with baseline data to help assess the extent and impact of perchlorate contamination in the Colorado River from Lake Mead to the Mexican Border. The sampling sites were selected from Tribal reservations where public water supplies were drawn from wells closest to the river and possibly recharged at least partially from the river.

The results all fall within the expected range when compared to results obtained last year. "In July 1997, monitoring of surface water sources in southern California showed perchlorate at low levels (5 to 9 ppb) in Colorado River water..." (source: California DHS website, http://WWW.DHS.CAHWNET.GOV/org/ps/ddwem/chemicals/perchl/perchlindex.htm). These most recent results also correlate with independent testing done by the Chemehuevi tribe in August 1997 which showed 6.7 ppb perchlorate in the river adjacent to their lands and was non-detect (<1 ppb) in their public water system supply wells. Furthermore, all of these results fall below the interim health standard of 18 ppb, adopted as an interim action level for drinking water by the State of California and as a provisional reverence dose for drinking water by the EPA, pending further scientific study.

The conclusion we may make in light of these results is that while the perchlorate levels do not pose a health risk at this time, a water quality monitoring program may need to be implemented to monitor the perchlorate levels in the Colorado River downstream from Lake Mead. If you have questions regarding these results, please call Karl Banks at 415-744-1849.

Drinking Water Office

Enclosure

Arizona Department of Environmental Quality California Department of Health Services Nevada Department of Human Resources Nevada Department of Conservation and Natural Resources

# Agency for Toxic Substance and Disease Registry - ATSDR (January 21, 1986):

"...Given the proprietary nature of the laboratory method for quantification and the poor quality assurance results noted, the data do not prove that perchlorate ion has actually been found. If the presence of perchlorate ion is confirmed, the scientific database on this ion is insufficient to generate either an acute or longer-term health advisory for drinking water"

"...The minimal acute toxicity data available suggest that one or two ppm perchlorate ion would not represent an imminently acute and substantial threat to the public health. The ATSDR does not consider this level to be "safe" in the absence of experimental data"

# **Perchlorate Toxicology**

### CDC, 1986 - Not Enough Data

### NCEA (Superfund), 1992

- Use as a Drug for Hyperthyroidism
- Inhibits Iodide Uptake (Radiolabel)
- 1952 Dose Study, Graves Patients
  - 100 mg Complete
  - 10 mg Minimal \* NOAEL
- Human Health Effects
  - Aplastic Amemia

#### **Uncertainty Factors**

- 10x for Lack of Chronic Effect Study
- 10x for Sensitive Population (e.g., Impaired Thyroid)
- 10x for Data Base Limitations

# **Perchlorate Toxicology**

### NCEA (Superfund), 1992 continued

- 10 mg \* NOAEL for 70 kg Human
- 1000x Uncertainty Factor
- Rounding to One s.f.
- Provisional Reference Dose:1 E-4 mg/kg-day

**Industry Protest: More Data Available** 

#### **NCEA 1995 Revision**

- Range 3x to 10x
   for Data Base Limitations
- Provisonal Reference Dose Range:
   1 E-4 to 4 E-4 mg/kg-day

In Drinking Water (2 I/day, 70 kg adult)

4 ug/l to 18 ug/l (ppb)

## **Perchlorate Toxicology**

Air Force and Industry Sponsored Toxicological Studies (Sept , 1997)

EPA will review/revise RfD October, 1998

Rancho Cordova epidemiologyUnconclusive
Looking at Newborn Thyroxin

# **Treatment Technologies**

Very High Oxidation Potential Very High Activation Energy

Chemical Reduction Unsuccessful (Iron, Sulfides, Palladium catalyst)

Bioremediation - drawbacks

Ion Exchange, Reverse Osmosis,
Nanofiltration - Drawbacks (cost, waste)

East Valley Water District...AWWARF (\$2 Million from EPA's OST Budget)

**Tech Support, Reviewing \$F Report** 

Other Efforts -San Gabriel, USAF, MWD

Areas of Scientific Uncertainty

STUDY	Н	Α	S	D	L	CRITICAL EFFECT
1. Developmental/ neurotoxicity	X			X		Neurobehavioral deficits due to toxicity to developing thyroid?
2. 90-day, all other organs				X		Thyroid as critical effect?
3. Receptor kinetics (in vitro	Х	X				Comparative human and rat discharge data?
studies)						
4. Segment II developmental				X		Gross and skeletal fetal abnormalities, fetal survival
5. ADME - Absorption,	Χ	X		X		Comparative studies must be done carefully
Distribution, Metabolism			Į	1		
and						
Elimination						
6. Mutagenicity/			X.	X		
Genotoxicity						
7. Reproductive				X		
8. Immunotoxicity				X		

H = AVG HUMAN TO SENSITIVE HUMAN

A = ANIMAL TO MAN

S = SHORT TERM TO LONG TERM STUDIES

L = LOAEL TO NOAEL

D = DATA BASE

Of these eight areas, it is essential to complete the 90-day study and the neurobehavioral developmental study in order to determine that the critical effect(s) of perchlorate has been identified. The remaining studies are useful for addressing a number of other uncertainties in the database. In addition, an in-depth review of the current literature on the toxicity of perchlorate compounds and on the comparative sensitivity of humans and rats to thyroid toxicants was recommended by the panel. This is currently in progress at Wright-Patterson Air Force Base. With this information, prepared (and once the present set of studies have been completed a complete summary of toxicological data can be). This will also enable the development of a proposed RfD on a more informed basis.

#### Studies, Cost and Time Frame

STUDY	Description	4Q97	1Q98	2Q98	3Q98	4Q98	~Cost (thosands)	Sponsor
I. Neurobehavioral Developmental	tests nervous system of fetal, newborn and young animals	X ·	х	х			350	USAF
2. 90-day, all other organs	tests many organs of young adult animals	х	х	х			350	USAF
3. Receptor kinetics (in vitro studies; perchlorate discharge tests)	tests for mechanism of toxicity	x	х				in house literature review	USAF
4. Segment II developmental	tests for birth defects		х	х			101*	PSG
5. ADME - Absorption, Distribution, Metabolism and Elimination a. Literature Review b. Kinetics Proposals c. Throid Mechanistic Study (3 phases)	compares how perc' lorate is absorbed, metaboli ed, and excreted in animals and humans	х	x	X X X	X X	х	Internal 200 (USAF) 150+ (RTP)	USAF/PSG NASA NASA
6. Mutagenicity/ Genotoxicity	tests for mutations and toxic effects on DNA		Х	X	<del> </del>		37	PSG
7. Reproductive	tests for reproductive performance in adults, and for toxicity in young animals		х	х	x	x	334*	PSG
8. Immunotoxicity	tests for immunotoxicity in adults			х	х	x	275	US Army

<sup>•</sup> Does not include the analysis of thyroid hormones. If needed, this work is estimated to cost between 55 and 85 thousand dollars.

#### Issues with Perchlorate

#### Existing uncertainties in:

- the toxicological database documenting its health effects at low levels in drinking water;
- 2) the actual extent of the occurrence of perchlorate in ground and surface waters;
- 3) the validation of the analytical detection method; and
- 4) the efficacy of available treatment technologies needed for drinking water.

One CANNOT equate lack of data (no data or insufficient data), with failure to support a possible cause and effect relationship.

Positive studies may support a relationship, but a negative study *DOES NOT* negate a possible relationship.

# Interagency Perchlorate Steering Committee



- Formed January, 1998
- EPA, Department of Defense, ATSDR, National Institute for Environmental Health Sciences (NIEHS), and state, tribal and local governments
- Occurrence, Health Effects, Treatability and Waste Stream Handling, Analytical Detection, Ecological Impacts, Regulatory Updates
- Information transfer and coordination